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Short communication

Electrical characterization of sol–gel-derived $(1-x)$NBT–xNTa $(0.05 < x < 0.3)$ thin films

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Abstract

Ferroelectric $(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$xNaTaO_3$ (NBT–NTa) thin films, with $0.05 < x < 0.3$, were deposited on a $Si/SiO_2/TiO_2/Pt$ substrate using a modified sol–gel method. The dielectric permittivity, the dielectric losses, the voltage-tunability and the ferroelectric behavior of the NBT–NTa thin films were investigated. The thin films with 5 mol% and 10 mol% $NaTaO_3$ showed a similar dielectric permittivity ($\varepsilon \approx 441$ at 1 MHz) and voltage-tunability ($n_r \approx 42\%$ at 370 kV/cm, 1 MHz), whereas the thin films with 30 mol% of $NaTaO_3$ had a lower dielectric permittivity ($\varepsilon \approx 370$) and voltage-tunability ($n_r \approx 23\%$). The relaxor-type ferroelectric response in the thin films with 5 mol% $NaTaO_3$ was due to a decrease in the average grain size to below 150 nm, resulting in the appearance of single-domain grains.

Keywords: A. Sol–gel processes; A. Films; C. Electrical properties; D. Perovskites

1. Introduction

Ferroelectric thin films have received a lot of research attention due to their integration into multifunctional devices [1–8]. Ferroelectric, lead-based materials are still in common use; however, the environmental pollution that accompanies the processing and waste disposal of these materials means that there is a requirement for alternative, lead-free materials, such as a bismuth sodium titanate compound.

Bismuth sodium titanate (NBT) has a relatively large remnant polarization $P_r = 38\ \mu C/cm^2$ at room temperature combined with a high Curie temperature (320 °C). Its drawbacks are a high conductivity and a large coercive field [1–3], which can be improved by the formation of a solid solution with other perovskite materials [4–8].

The investigated bulk $Na_{0.5}Bi_{0.5}TiO_3$–$NaTaO_3$ (NBT–NTa) ceramics have shown very large changes in their dielectric and ferroelectric properties, as well as in their voltage-tunable characteristics, with an increase in the $NaTaO_3$ (NTa) concentration [9,10]. Thin films with the composition 70 mol% NTa + 30 mol% NTa have already been prepared using a sol–gel synthesis and the processing parameters, such as the pyrolysis and annealing temperatures, were found to have a significant influence on the phase and microstructural development [11]. In particular, the formation of the undesirable pyrochlore phase in thin films was observed to be dependent on the pyrolysis conditions [11]. The reported dielectric properties of NBT–NTa thin films were measured in the radio (RF) and microwave (MW) frequency ranges [11], though only for the composition with 30 mol% NTa. However, studies on other electrical characterizations of NBT–NTa thin films, such as the tunability or the ferroelectric response, have not been reported so far.

It was reported that using metal precursors with longer carboxylate chains can promote the formation of the perovskite phase [12,13]. Studies of bismuth-based compounds [14] have shown that a Bi-precursor with longer carboxylate chains, due to its low decomposition temperature, can expedite the formation of Bi-based compounds. Based on these reports [12–14], we have used the Bi-propionate precursor for the preparation of NBT–NTa

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thin films with sol–gel synthesis. Nevertheless, the focus of this study will be on an electrical characterization of NBT–NTa thin films, in particular with compositions up to 30 mol% of NTa, which in bulk form show the greatest diversity in electrical responses.

2. Experimental

The precursor solutions of $(100-x)$NBT–xNTa with $x=5$, 10 and 30, identified as 5NTa, 10NTa and 30NTa, respectively, were prepared by dissolving titanium n-butoxide ($Ti(OC_3H_7)_4$, Alfa Aesar, 98+%) and tantalum ethoxide ($Ta(OC_2H_5)_5$, Alfa Aesar, 99+%) in a mixture of 2-metoxyethanol $C_3H_8O_2$, Alfa Aesar) and acetylacetone (AcAc) ($C_5H_8O_2$, Alfa Aesar), where the molar ratio of the Ti:AcAc=1:2 and Ta:AcAc=1:1. The AcAc was added to prevent the hydrolysis of metal alkoxides caused by moisture in the air. Afterwards, the sodium acetate ($NaOOCH_3$, Alfa Aesar, 99%) was added to the Ti–Ta-solution and mixed until dissolution. The required amount of bismuth oxide (Bi_2O_3, Alfa Aesar, 99%) was dissolved in the propanoic acid ($C_3H_6CO_2$, Alfa Aesar) at 120 °C and refluxed for 3 h to form Bi-propionate, which was added to the Na–Ti–Ta-solution after cooling. A 5 wt% excess of sodium and bismuth precursors were introduced to compensate for their evaporation during the high-temperature annealing. The mixture was stirred and heated at 80 °C for 2 h to obtain a clear yellow precursor solution with a concentration of 0.4 M.

The precursor solution was filtered to remove dust particles using 0.2-μm PTFE syringe filters and then spin coated on a $Si/SiO_2/TiO_2/Pt$ substrate at 3000 rpm for 30 s. A two-step pyrolysis was implemented in which each coating was dried at 200 °C for 5 min and then at 450 °C for 30 min. After a total of 10 layers the thin films were rapidly heat treated at temperatures between 600 °C and 700 °C for 30 min.

The phase composition was monitored by X-ray powder diffraction (XRD) (D4, ENDEAVOR, Bruker Axs) and the microstructure development of the films was investigated with field-emission scanning electron microscopy (SEM) (ULTRA ULTRA Plus, Carl Zeiss NTS GmbH, Oberkochen, Germany). The average grain size was obtained from XRD patterns using the program Topaz 2R (Bruker AXS, version 2.0, Release 2000). The electrical characterization was made using a Probe station (Summit 12000AP, Cascade Microtech, USA) and a microprobe DCP115R (Cascade Microtech, USA). Top gold electrodes with ϕ 200 μm were deposited on thin films by sputtering. For the dielectric properties and the tunability measurements a Precision LCR meter (Agilent 4284A, Agilent Technologies, USA) was used in the frequency range 1 kHz to 1 MHz at room temperature. The maximum voltage used for the tunability measurements was 20 V, which corresponds to an electric field of 370 kV/cm, for 550-nm-thick films. The (P–E) hystereses were measured using a Radiant Precision LC meter with a TTI QL564P power supply, at 1 Hz, 9 V and room temperature.

3. Results & discussion

The results of the XRD analyses of the $(100-x)$NBT–xNTa thin films with $5<x<30$ showed the formation a single perovskite phase for each annealing temperature used. The XRD analyses of the 5NTa, 10NTa and 30NTa thin films annealed at 700 °C/30 min are shown in Fig.1. The FE-SEM micrographs of the 10NTa thin film heat treated at different temperatures are shown in Fig.2. It is clear that the thin films have a dense, homogeneous microstructure consisting of nanograins. A similar microstructure development with increasing annealing temperature was also obtained for the 5NTa and 10NTa thin films. The average grain sizes of the 5NTa, 10NTa and 30NTa thin films annealed at different temperatures are given in Table 1. The estimated thickness for all the thin films was 550 nm.

The dielectric permittivity and the dielectric losses of the 5NTa, 10NTa and 30NTa thin films, annealed at 600 °C, 650 °C and 700 °C, were measured as a function of the frequency (1 kHz to 1 MHz) at room temperature, as shown in Fig. 3. Regardless of the composition and the annealing temperature, in all the thin films we observed a linear decrease in the dielectric permittivity with frequency. For the 5NTa thin films a noticeable increase in the permittivity with the annealing temperature occurs from $\varepsilon=325$ at 600 °C to $\varepsilon=439$ at 650 °C, and afterwards a minor increase to $\varepsilon=441$ at 700 °C (1 MHz). This increase of the dielectric permittivity between 600 °C and 650 °C we ascribed to the abrupt increase of the average grain size from 73 nm to 95 nm (Table 1). Afterwards, the improvement in the dielectric permittivity value as small, as the average grain size only grew to 106 nm at 700 °C. The obtained dielectric permittivity values for the 10NTa thin films were 400, 410 and 440 (1 MHz) for 600 °C, 650 °C

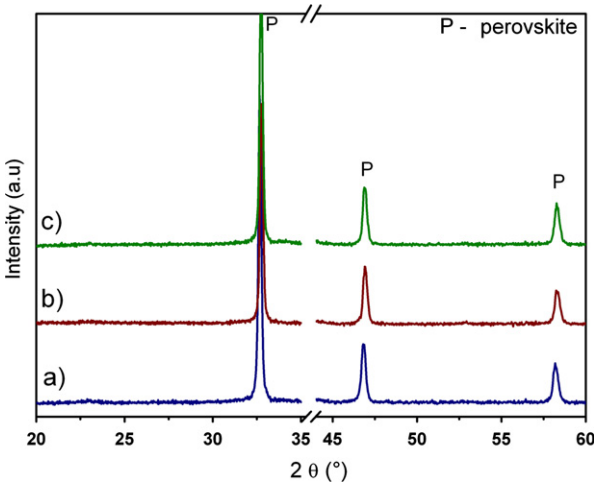

Fig. 1. XRD results of the thin films (a) 5NTa, (b) 10NTa and (c) 30NTa, annealed at 700 °C.

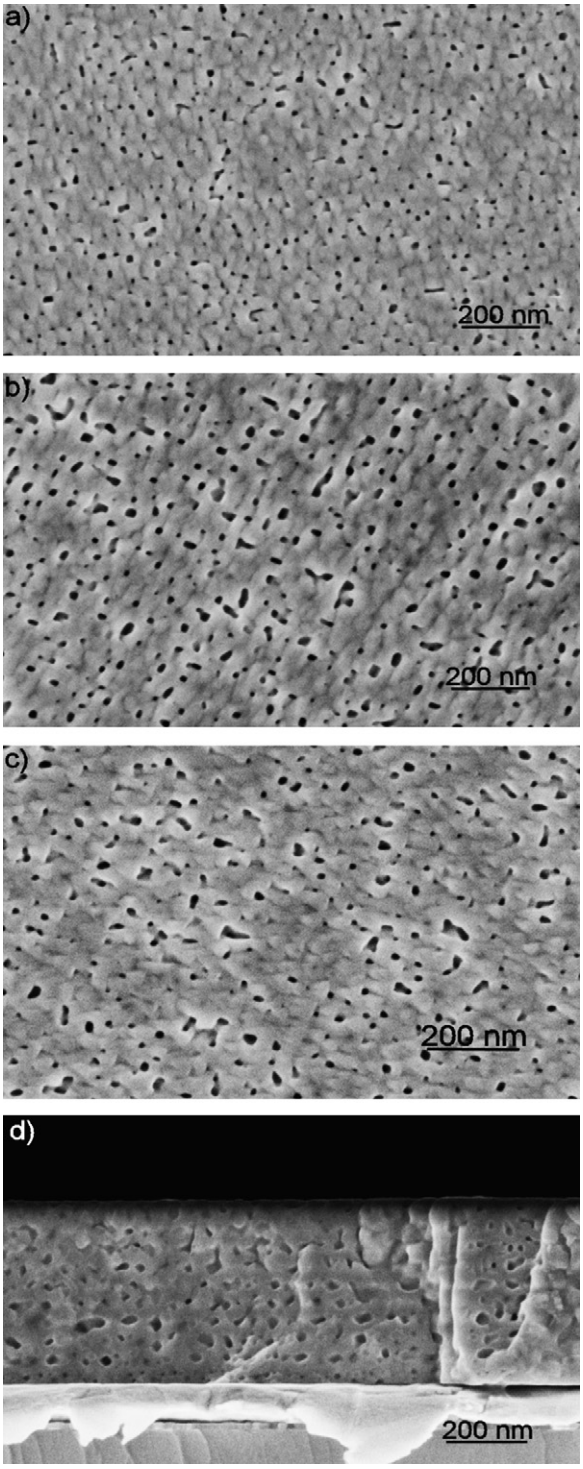

Fig. 2. SEM images of the 10NTa thin film annealed at (a) 600 °C, (b) 650 °C, (c) 700 °C and (d) 700 °C; cross-section.

and 700 °C, respectively. Such minor improvements in the dielectric permittivity for the 10NTa thin films originate from a small increase in the average grain size with the annealing temperature (Table 1). For the 30NTa thin films the average grain size hardly changes between the annealing temperatures of 600 °C (90 nm) and 650 °C (96 nm), resulting in a small improvement of the dielectric

Table 1
NBT–NTa thin films' average grain size as a function of the annealing temperature.

Temperature (°C)	Crystallite size (nm)		
	5NTa	10NTa	30NTa
600	73 ± 14	87 ± 18	90 ± 12
650	95 ± 14	94 ± 20	96 ± 18
700	106 ± 20	100 ± 20	110 ± 18

permittivity values $\varepsilon = 292$ and $\varepsilon = 305$, respectively. However, the increase in the average grain size to 110 nm at 700 °C increases in the dielectric permittivity to $\varepsilon = 370$. The same dependence of the dielectric permittivity with increasing annealing temperature can also be observed for all the thin films at frequencies below 1 MHz. The dielectric losses, regardless of the annealing temperature, remain fairly constant and below 5×10^{-2} for the whole frequency range.

The hysteresis loops of the 5NTa, 10NTa and 30NTa thin films annealed at 700 °C are shown in Fig. 4. The 5NTa and 10NTa thin films both exhibit a slim hysteresis loop, which is usually obtained for relaxors, whereas the 30NTa thin film's hysteresis loop shows characteristic paraelectric behavior. A remnant polarization (Pr) of 2.5 μC/cm^2 and a coercive field (Ec) of 12 kV/cm were obtained for the 5NTa thin film, whereas the 10NTa thin film had Pr = 1.7 μC/cm^2 and Ec = 8 kV/cm. The 30NTa thin films showed Pr = 0.7 μC/cm^2 and Ec = 2 kV/cm.

Both the 10NTa and 30NTa thin films displayed the expected ferroelectric responses, i.e., the relaxor- and paraelectric-type, but the relaxor-type response for the 5NTa thin film diverges from the ferroelectric-type observed in the bulk contra part [10]. In ferroelectric systems [15–17] when the grain size decreases below 200–300 nm, the multi-domain structure changes to a single domain, which requires a higher activation energy for the reorientation of the domain and consequently affects the polarization aptitude of the ferroelectric material. Therefore, the difference in the ferroelectric responses between the bulk and the thin film with 5 mol% of NTa is caused by the presence of the single-domain grains, as the thin film's average grain size is approximately 106 nm.

The variation of the dielectric data as a function of the composition and the annealing temperature is presented in Table 2. It is clear that for the NBT–NTa thin films the relative tunability ($n_r = \varepsilon(0) - \varepsilon(E)/\varepsilon(0)$) increases with an elevated annealing temperature. The 5NTa and 10NTa thin films show a comparable voltage-tunability inclination (Fig.5), as their obtained relative tunability values are almost the same and are between 37% and 42% for the lowest to the highest annealing temperature (Table 2). Such a result is due to the relaxor type-nature and comparable dielectric permittivity values of both thin films. The paraelectrical 30NTa thin films display a lower voltage-tunability tendency (Fig.5), as the relative tunability values range from 21% to 23% with increasing

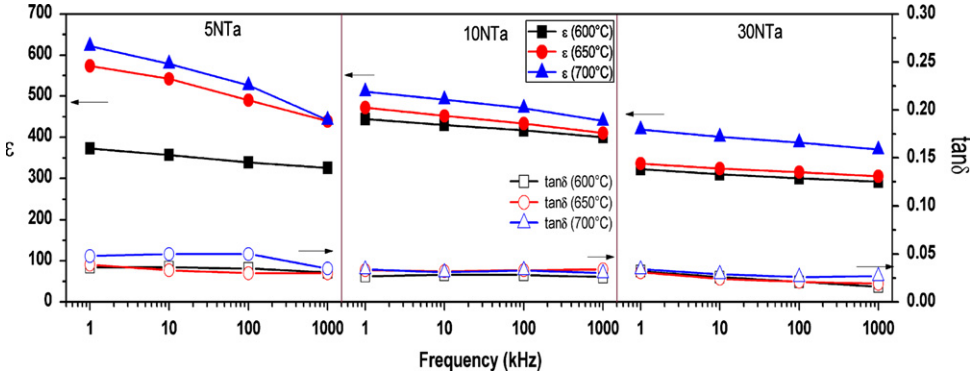

Fig. 3. Dielectric permittivity and dielectric losses as functions of the frequency and annealing temperature.

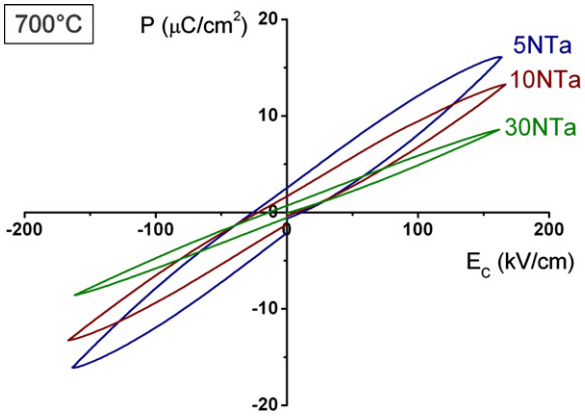

Fig. 4. Hysteresis loops of the 5NTa, 10NTa and 30NTa thin films, annealed at 700 °C, measured at 1 Hz, 9 V and room temperature.

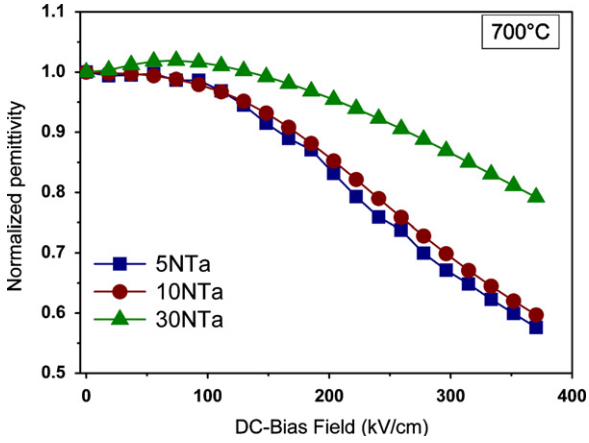

Fig. 5. DC-bias field dependence of the normalized permittivity of the 5NTa, 10NTa and 30NTa thin films, annealed at 700 °C. Data were obtained at 1 MHz and room temperature.

Table 2
Variation of the dielectric data[a] with the composition and annealing temperature.

Thin films	Annealing temperature (°C)	n_r (%)	ε (0) (/)	tanδ (/)
5NTa	**600**	**37**	**325**	**0.03**
	650	**39**	**439**	**0.03**
	700	**42**	**441**	**0.03**
10NTa	**600**	**37**	**400**	**0.03**
	650	**39**	**410**	**0.03**
	700	**40**	**440**	**0.03**
30NTa	**600**	**21**	**292**	**0.02**
	650	**22**	**305**	**0.03**
	700	**23**	**370**	**0.03**

n_r—relative tunability measured at 370 kV/cm.
ε(0)—dielectric permittivity at 0 DC-bias field.
tanδ—dielectric losses.
[a]Measured at room temperature and 1 MHz.

temperature (Table 2). The voltage-tunability values of the 30NTa thin films show a remarkable decrease compared to the bulk ceramic [10] and are closer to the values for ceramics with a $NaTaO_3$ content above 50 mol% [10], which are known to possess smaller volume fractions of the polar nano-regions. Therefore, the low tunability values of the 30NTa thin films indicate a considerably reduced amount of the polar nano-regions.

4. Conclusions

In the present study we characterized the electrical properties of $(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$xNaTaO_3$ thin films ($0.05 < x < 0.3$) prepared by a modified sol–gel method. A dense and homogenous microstructure, with the average grain size ranging between 70 and 110 nm, was obtained for the NBT–NTa thin films by using a Bi-propionate precursor in the sol–gel synthesis. It was observed that the dielectric permittivity increases with the annealing temperature for all the prepared NBT–NTa thin-film compositions. The decrease in the average grain size below 150 nm caused the appearance of single-domain grains, which then strongly affected the polarization behavior of the 5NTa thin films, giving them a relaxor-type response. The relaxor-type and paraelectric-type responses were observed for the 10NTa and 30NTa thin films, respectively. Comparable dielectric permittivity and relative tunability values were obtained for the 5NTa ($\varepsilon = 441$, $n_r \approx 42\%$) and the 10NTa ($\varepsilon = 440$, $n_r \approx 40\%$) thin films, whereas the 30NTa thin films showed lower values ($\varepsilon = 370$, $n_r \approx 23\%$).

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